Fuel Processing Technology 153 (2016) 101–110

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Effects of sample preparation on the accuracy of biomass content determination for refuse-derived fuels

Therese Schwarzböck *, Philipp Aschenbrenner, Helmut Rechberger, Christian Brandstätter, Johann Fellner

Institute for Water Quality, Resource and Waste Management, TU Wien, Karlsplatz 13, E226/2, 1040 Vienna, Austria

ARTICLE INFO

Article history:
Received 5 April 2016
Received in revised form 29 June 2016
Accepted 1 July 2016
Available online 4 August 2016

Keywords:
Biomass content
Refuse-derived fuels
adapted Balance Method
Sample preparation
Variance component analysis

ABSTRACT

A reliable and practical method for characterizing refuse-derived fuels (RDF) with respect to greenhouse gas-relevance (or biomass content) is required by industries and waste management companies. As RDF usually consist of a variety of materials with different physical properties, sampling and sample preparation may represent crucial steps with regard to reliable analysis results. This is particularly valid for analytical methods, which rely on only small test specimens (centigrams), such as the adapted Balance Method (aBM). The aBM was recently developed by the authors and is based on elemental analyses (CHNSO). The investigations focus on elaborating an appropriate sample preparation for the aBM. To this end, two RDF model mixtures are generated out of paper, cardboard and different plastics, and comminuted down to a grain of size of <0.2 mm using two differing mills as finishing step. The results of the aBM (applied for 52 samples) show that the performance of the method in terms of trueness and variation is competitive relative to standardized methods. Deviations between the determined value and the theoretical biogenic mass fraction are below 4.5%rel (at a probability of 95%). Furthermore, the standard deviation for both mixtures is below ±3.0%rel. A nested variance component analysis indicates that the last milling step and the step of drawing the test specimens for analysis contribute most to the observed variability. A consecutive application of two types of mills as a finishing step prior to analysis is proposed in order to facilitate a sufficient grinding of plastics as well as of cellulose fibers.

1. Introduction

Energy recovery from wastes and refuse-derived fuels (RDF) has become of increasing importance for energy-intensive industry branches such as cement manufacturing. In Austria this development has been strongly facilitated by the implementation of the landfill directive in 2009, which bans the disposal of waste with a total organic carbon content larger than 50 g/kg or a lower calorific value above 6.6 MJ/kg waste [1]. Thus, materials of high calorific value present in wastes such as plastics, paper, cardboard or textiles are separated in mechanical-biological pre-treatment plants and are subsequently utilized as RDF in industrial plants, thereby substituting conventional fuels. According to the Association of Austrian Cement Industry, the share of refuse-derived fuels in the European cement industry reached a level of 34% by 2012 [2]. In Austria in 2014 already 75.5% of the energy required in cement works stem from secondary fuels [2]. These fuels are, on the one hand, associated with several benefits for the operators: they are usually cheaper, domestically available, and usually less CO_2 intensive than conventional fuels (e.g. coal) [3,4]. However, their utilization goes along with various challenges. Probably the biggest challenge for producers and operators is the heterogeneity of the fuel, which requires reliable, practical and cost effective methods to characterize their quality and thus the environmental aspects associated with their thermal utilization. Besides the compulsory parameters according to EN 15359:2011 [5] (calorific value, content of chlorine and heavy metals), other specifications like, phosphorous content or the biomass content are becoming of increasing importance with respect to the quality and economic value of solid recovered fuels (SRF, which are RDFs produced in accordance with European Standards). The European Recovered Fuel Organization, for example, addresses the significance of determining

Abbreviations: A, ash content; aBM, adapted Balance Method; CV, coefficient of variation (related to the mean); HD-PE, high-density polyethylene; MS, mean sum of squares; n, number of analyses; N, number of analysis samples; PET, polyethylene terephthalate; PS, polystyrene foam; RDF, refuse-derived fuel; RSD, relative standard deviation (related to the mean); SD, standard deviation; SRF, solid recovered fuel; SS, sum of squares; TIX_{wf}, total inorganic content of the respective element in the water-free ignition residue; TOC, total organic carbon; TOH, total organic hydrogen; TON, total organic nitrogen; TOO, total organic oxygen; TOS, total organic sulfur; TOCl, total organic sulfur; TOX_{waf}, total organic content of the respective element in the water-and-ash-free sample; TX_{wf}, total content of the respective element in the water-free sample; UCM, ultra-centrifugal mill; VCA, variance component analysis; waf, water-and-ash-free; wf, water-free; wt%, percentage by weight; x_B, biogenic matter; $x_{B,aBM}$, biogenic mass fraction determined by the adapted Balance Method; $x_{B,Theory}$, theoretical biogenic mass fraction; x_F, fossil matter; σ^2rel., relative variance component (related to the overall variance); σ^2, variance component.

* Corresponding author.
E-mail address: therese.schwarzboeck@tuwien.ac.at (T. Schwarzböck).

http://dx.doi.org/10.1016/j.fuproc.2016.07.001

the biomass content in SRF for the sake of reducing greenhouse gas emissions through the substitution of fossil fuels [6].

Both producers and users of RDF are interested in reliable and cost-effective methods for characterizing the fuel in terms of greenhouse gas-relevance. Until now, three methods to determine the biomass content in SRF have been described in the standard EN 15440:2011 [7], namely the manual sorting method, the selective dissolution method, and the radiocarbon method. All three methods are commonly applied (for example [8–12]). In addition to the standardized methods, the Balance Method has been developed and implemented in various waste-to-energy plants in recent years and is currently in the last stage of standardization [13–16]. This method combines standard data on the chemical composition of biogenic and fossil organic matter with routinely measured operating data from waste-to-energy plants and has been demonstrated as a reliable method with very low costs in comparison to alternative methods [16,17]. However, the Balance Method does not allow a characterization of the fuel before its utilization as it employs post-combustion data. Hence, the authors have developed a laboratory-based analysis method – the so-called adapted Balance Method (aBM) – which shows promising results [18,19]. Analyses of defined mixtures of biogenic (like cardboard and wood) and fossil materials (like polyethylene and polystyrene) revealed deviations from the theoretical value of below 1% when the materials were mixed after milling [20]. When materials were mixed prior to the sample preparation, results of the aBM differ by <5% (relative) from the known composition of a two-component mixture consisting of paper and polyethylene [19].

However, waste materials are typically strongly heterogeneous with respect to their physical properties and texture and thus, different steps during sampling, sample processing, and analysis can be critical factors for a reliable analysis result [21]. Due to different material characteristics, the components of the mixture may behave differently when it comes to comminution or sample size reduction. Hence, besides sampling, the sample preparation needs careful attention in order to ensure correct and reproducible analysis results. This is particularly valid when only very small test specimens are required for the analysis. For example, the adapted Balance Method (which relies on the elemental analysis) or the radiocarbon method depends on the analysis of only a few milligrams or centigrams per measurement.

Hence, the aim of the investigations presented in this paper is to elaborate an appropriate sample preparation procedure in order for the adapted Balance Method (aBM) to achieve highly reproducible results. In particular, the following aspects are addressed:

- Determination of the reliability of the aBM in terms of accuracy and precision (by means of predefined RDF model mixtures)
- Evaluation of the influence of different sample preparation steps on the final result of the aBM (hierarchical experimental set-up)
- Identification at which layer of the analysis procedure (different sample conditioning steps and chemical analysis) most of the efforts should be concentrated in order to avoid/minimize potential errors
- Identification of approaches for optimizing the conditioning procedure (comparison of different milling strategies).

2. Materials and methods

Within the framework of the present study the biomass content of two predefined material mixtures with different composition and different heterogeneity is determined using the adapted Balance Method (aBM) (Fig. 1). Mixture I consists of paper and polyethylene, whereas mixture II is made out of paper, cardboard, polyethylene, polyethylene terephthalate and polystyrene. A special focus is given to the effects of the sample preparation on the final analysis results, different comminution steps are applied and evaluated using various statistical methods, such as the variance component analysis (VCA). For the latter in particular, a hierarchical experimental set-up is chosen, meaning that after each conditioning step replicate samples are produced.

2.1. Determination of the biomass content using the adapted Balance Method

The adapted Balance Method (aBM) relies on the distinctly different chemical composition of water-and-ash-free biogenic and fossil organic matter, where fossil in this context is understood as materials produced out of crude oil, natural gas or coal.

The necessary input data for the calculation are derived from elemental analyses (CHNSO). Additional data on the chemical composition of the water-and-ash-free biogenic and fossil matter are required, which can be derived from literature or from separate analyses of pure biogenic and fossil organic matter present in the fuel (see [18]). Mass balance equations are set up for carbon, hydrogen, nitrogen, sulfur and oxygen. Each balance equation contains the two unknown mass fractions of fossil and biogenic matter (x_B and x_F). As an example, the two pie charts on the left in Fig. 2 show the elemental composition of water-and-ash-free biogenic and fossil matter present in municipal solid waste (total organic carbon TOC, total organic hydrogen TOH, total organic nitrogen TON, total organic sulfur TOS, total organic oxygen TOO and total organic sulfur TOCl) (data as given in [17]). By multiplying these compositional data by the respective mass fractions of waf biogenic organic matter (x_B) and fossil organic matter (x_F), the composition of the material mixture (or RDF) is obtained (pie chart on the

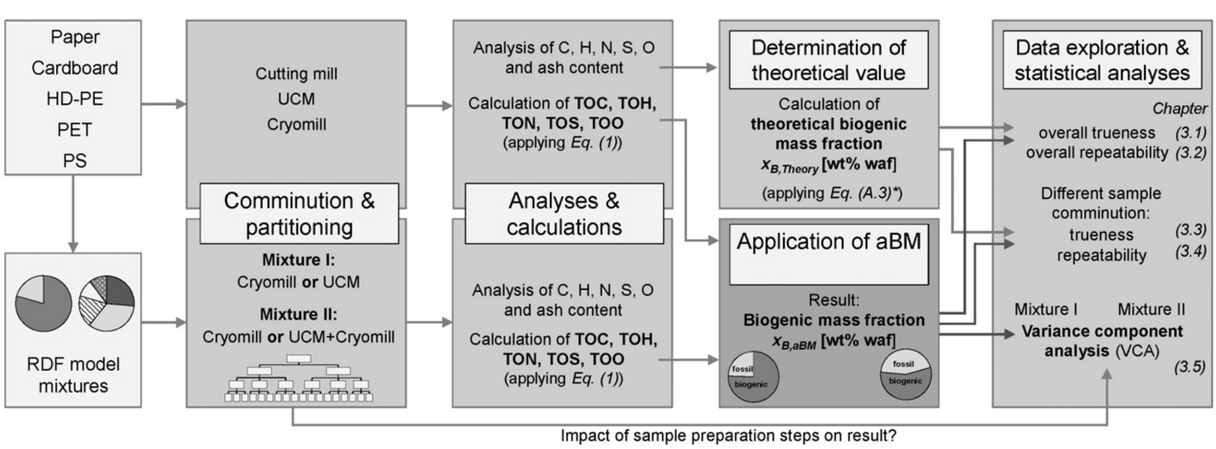

Fig. 1. Schematic illustration of the procedure chosen for the investigations conducted: application of the adapted Balance Method (aBM) to two different predefined RDF model mixtures and evaluation of the impact of different comminution steps on the final results.

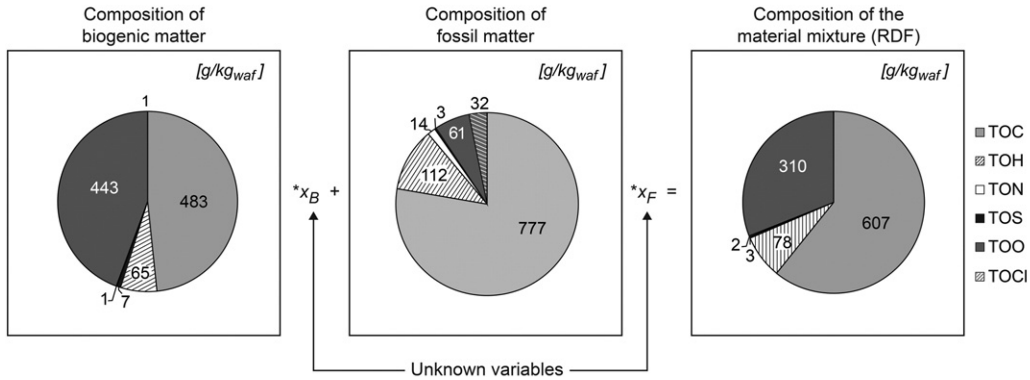

Fig. 2. Schematic illustration of the adapted Balance Method, showing the relation between the chemical composition of biogenic and fossil organic matter and the material mixture (all on a water-and-ash-free basis - waf); for each element (TOC, TOH, TON, TOS, TOO, TOCl; presented data are for municipal solid waste given in [17]) a balance equation is set up to determine the unknown variables: mass fraction of biogenic matter x_B [wt% waf] and mass fraction of fossil matter x_F [wt% waf].

right in Fig. 2). The set of five balance equations is overdetermined (more equations than unknowns), thus a data reconciliation algorithm based on non-linear optimization can be applied to reveal the quantity of the unknown mass fractions (biogenic x_B, fossil x_F). The basic balance equations of the adapted Balance Method are provided in the Supplementary material section C.; further details are given in [18].

2.2. RDF model mixtures

For the preparation of the two predefined RDF model mixtures, the following biogenic and fossil materials are used:

Biogenic materials:

- cardboard: packaging, double walled
- paper: 80 g/m^2, Antalis Austria GmbH and 150 g/m^2, Inkjet Paper, Canon

Fossil materials:

- high-density polyethylene (HD-PE): laboratory grade HD-PE bottles, 250 ml, SciLabware
- polyethylene terephthalate (PET): cleaned PET-bottles without label, 237 ml, SPAR AG
- extruded polystyrene foam (PS): insulation boards, Austrotherm GmbH.

All chosen materials are usually represented in RDF made out of municipal solid waste and commercial waste in a high proportion [22–24] and are characterized by different physical behaviors (e.g. thermal stability, density). Paper and cardboard are considered to be biogenic matter, whereas HD-PE, PET and PS represent fossil materials (produced out of crude oil). All materials are shredded down to a grain size of <4 mm by a cutting mill (Retsch SM 2000). Two material mixtures of different composition regarding the biomass content are prepared out of the <4 mm materials. The respective amounts of the different materials are weighed with an electronic balance (Sartorius Extended, Sartorius Mechatronics) and filled into a 60 l container. The mixtures are thoroughly mixed by shaking the container in circular motions for about 10 min.

Based on the share of the biogenic and fossil materials and their ash content (as determined by analyses), the theoretical biomass fraction for the mixtures is calculated on a water-free (wf) and water-and-ash-free (waf) reference basis (equations are given in the Supplementary material, Eqs. A.1 to A.4). Table 1 summarizes the respective shares of the used materials and the theoretical biogenic mass fraction of both mixtures. The biogenic mass fraction on a water-and-ash-free basis $x_{B,Theory}$ of mixture I is 75.5 wt% waf and mixture II holds 55.9 wt% waf (calculation available in Supplementary material - Eq. A.3).

2.3. Sample comminution and partitioning

For the CHNSO elemental analysis a final sample size of only a few centigrams is required. Thus, different sample preparation steps (comminution, partitioning) are necessary. The sample preparation is carried out in accordance with the Norm EN 15413:2011 [25].

The material mixtures undergo the sample comminution and segregation steps as outlined in Fig. 3. At each layer of conditioning replicate samples are produced. The first splitting of the mixture takes place at a grain size of <4 mm by using a riffle divider (Rational Kornservice 5 l with 18 splits at 19.1 mm each) resulting in two divided parts with each around 300 or 600 g. Afterwards the grain size is reduced to <1 mm using a cutting mill (Retsch SM 2000). The thereby observed sample loss is below 7 g (~1.8 wt% of the initial mass).

Once the <1 mm sample is obtained, two different mills are used to further reduce the particle size - a high-speed rotor mill (UCM, ultra-centrifugal mill, Retsch ZM 200) or a cryogenic mixer mill (Cryomill, Retsch). Both mills are commonly applied to reduce the particle size of waste samples (e.g.: [26–28], [29] – plastic, [30] – polymers). The Cryomill is preferably used for materials with a high share of plastics because the milling bin is cooled by liquid nitrogen in order to embrittle the material and thereby support the crushing of elastic particles (rather than plating them). However, the Cryomill has no provisions to generate samples of defined particle sizes, while the particle size of

Table 1
Composition of the RDF model mixtures.

	Biogenic materials		Fossil materials			Theoretical biogenic mass fraction in the mixture $x_{B,Theory}$	
	Paper wf [wt%]	Cardboard wf [wt%]	HD-PE wf [wt%]	PET wf [wt%]	PS wf [wt%]	wf [wt%]	waf [wt%]
Mixture I (600 g)	79.4	–	20.6	–	–	79.4	**75.5**
Mixture II (1200 g)	26.4	34.3	18.8	10.3	10.2	60.7	**55.9**

wf = water-free.
waf = water-and-ash-free.
wt% = wt% percentage by weight (ratio of mass to total mass).

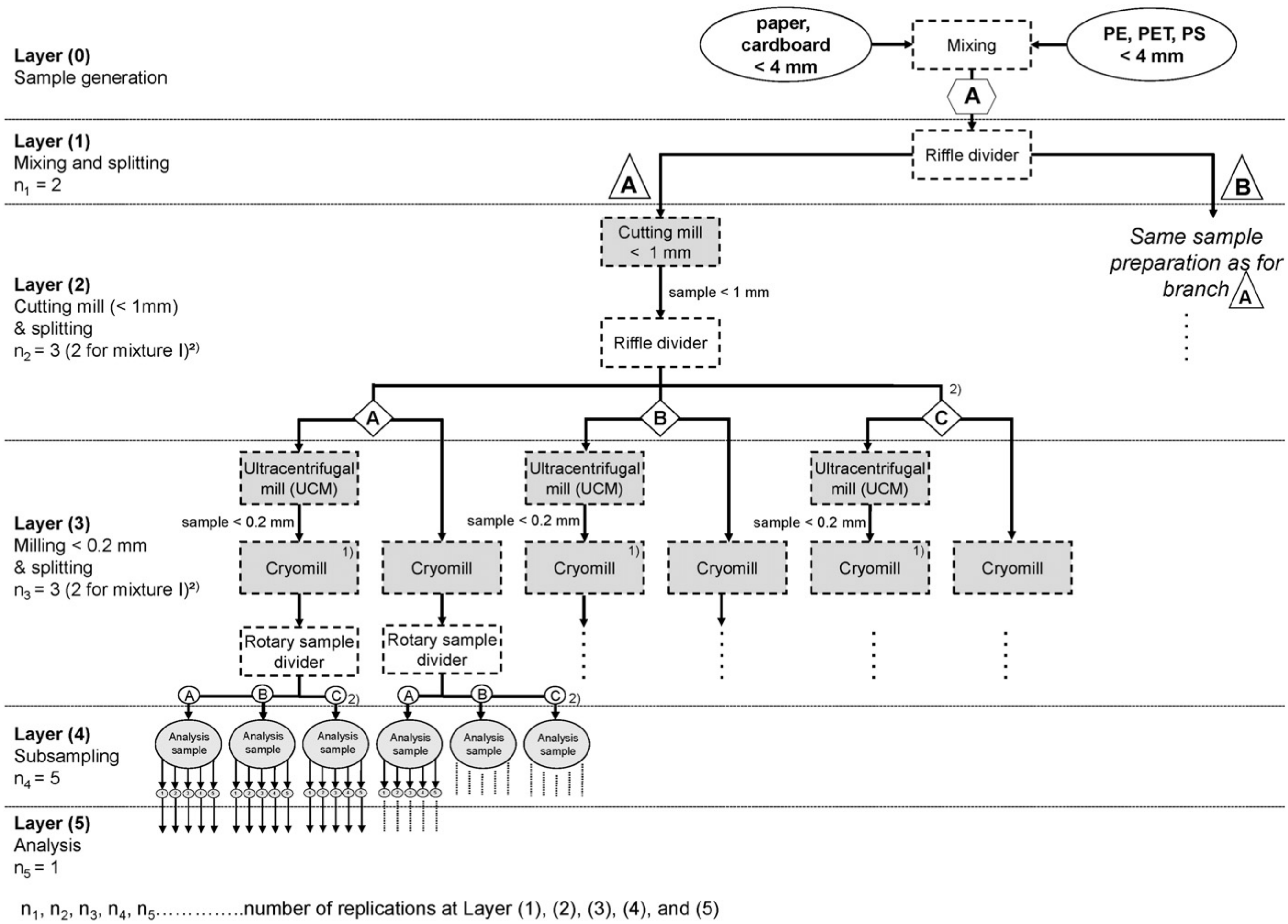

Fig. 3. Scheme of the sample conditioning (comminution and partitioning steps); note that the divided samples at each layer are illustrated in different shapes 1) The Cryomill-milling step after UCM-milling is only done for mixture II (not for mixture I); 2) For mixture I only two replications are done at each layer (no C-branches at Layer (2) and Layer (3) are produced).

comminuted materials via UCM is controlled by screens of defined dimensions. The performances of the two different mills are compared within this study to identify approaches for optimizing the conditioning procedure in terms of trueness and precision of the final results.

For mixture I (two-component mixture) the <1 mm fraction is milled down to <0.2 mm using either the ultra-centrifugal mill (UCM) or the Cryomill. The chosen test set-up for mixture II (five-component mixture) is partly based on results for mixture I (e.g. better performance of the Cryomill in terms of variance and trueness; see Sections 3.3 and 3.4). Thus, this mill is also used to comminute one half of mixture II. However, the other half of the samples are milled by the UCM and subsequently crushed into fine powder by the Cryomill prior to analysis (see Fig. 2 Layer (3)). Thus, two different milling procedures for each mixture are applied. The material losses from UCM-milling amount to 5.3 wt% on average, whereas the Cryomill causes lower losses in the range of 1.1 wt%. In order to receive replicate samples on Layer (3), a rotary sample divider (Retsch PT 100) is used, resulting in two (mixture I) or three (mixture II) analysis samples. All devices are cleaned carefully before each sample processing.

The splitting steps at each layer of comminution finally result in 16 analysis samples of mixture I (8 UCM-samples, 8 Cryomill-samples) and 36 samples of mixtures II (18 UCM + Cryomill samples, 18 Cryomill-samples), each of them holding 11 to 16 g.

The "pure" biogenic and fossil materials (paper, cardboard, HD-PE, PET, PS) are also comminuted down to <0.2 mm and subsequently their ash content and elementary composition (C, H, N, S, O) is determined in analogy to the material mixtures (see Section 2.4). Finally, the data obtained by the analyses of the single biogenic and fossil materials are aggregated to the elementary composition of waf biogenic and fossil organic matter present in mixture I and mixture II (see Supplementary material Table D.3), which serve as input data for the aBM.

2.4. Chemical analyses

2.4.1. Water content and ash content

For each analysis sample (Layer (4)) the water content and ash content is analyzed in duplicate and in accordance with EN 15414-3:2011 [31] and EN 15403:2011 [32]. To this end, 4 g material of each sample are dried at 105 °C for 24 h before being combusted at 350 °C in a muffle furnace for 1 h and at 550 °C for 4 h under air injection. All weights of the sample (before drying, after drying, after ignition) are recorded (using a mechanical balance 2432, Sartorius Mechatronics) in order to calculate the water and ash content.

2.4.2. Elemental analysis

The water-free (dried at 105 °C for 24 h) analysis samples (Layer (4)) are analyzed for the elemental composition (content of C, H, N and S) using an Elementar Macro instrument (Elementar Analysensysteme GmbH, Hanau, Germany). At a combustion temperature of 1150 °C, the total carbon TC, total hydrogen TH, total nitrogen TN, and total sulfur TS content are determined according to DIN 51732:2014 [33]. Five measurements per sample are carried out, each of them comprising 40 mg of sample material.

The total oxygen content TO is determined using an Elementar Vario EL instrument (Elementar Analysensysteme GmbH, Hanau, Germany). The analysis is based on the pyrolysis of the sample at 1150 °C and the conversion of all oxygen into CO. Compared to the CHNS-analysis, for each O-measurement only 4 mg of sample mass can be analyzed (due to limitations of the analyzer, allowing maximum 2 mg oxygen absolute). Due to the smaller sample size for oxygen analysis, seven measurements per sample are carried out. The uncertainties given by the device specifications are 0.5%rel for the CHNS-combustion analysis and 0.2%abs for the O-analyzer.

In addition, the ignition residue of each test sample treated in the muffle oven is analyzed for its elemental composition to appraise the total inorganic content of carbon, hydrogen, nitrogen, sulfur and oxygen. The values measured are converted according to Eq. (1) in order to receive the elemental composition of the analysis sample on a water-and-ash-free reference base.

$$\mathrm{TOX_{waf}} = (\mathrm{TX_{wf}} - \mathrm{TIX_{wf}} * \mathrm{A})/(1-\mathrm{A}) \tag{1}$$

whereby $\mathrm{TOX_{waf}}$ [g/kg] represents the total organic content of the respective element (C, H, N, S, O) in the water-and-ash-free sample, $\mathrm{TX_{wf}}$ [g/kg] the total content of the respective element in the water-free sample as measured, $\mathrm{TIX_{wf}}$ [g/kg] the total inorganic content of the respective element in the water-free ignition residue as measured, and A [kg/kg] the ash content (see also [19]). The thereby obtained values for total organic carbon TOC, total organic hydrogen TOH, total organic nitrogen TON, total organic sulfur TOS, and total organic oxygen TOO represent the main input parameter required for the adapted Balance Method (values are given in Supplementary material Table D.4). In addition, the contents of TOC, TOH, TON, TOS and TOO for the biogenic and fossil organic matter present in the mixture are required as input data for the aBM (see Supplementary material: Eqs. (B.1) and (B.2) and Table D.3).

2.5. Statistical tests

Statistical tests are carried out in order to evaluate differences between data sets regarding their central tendencies (means) and variances. All tests are carried out using the program R (Version 3.0.2) [34] or DataLab (Version 3.530) [35]. In particular, the following tests are applied:

- Shapiro test: test for normal distribution (required to decide which subsequent statistical test, e.g. *t*-test, Kruskal-Wallis test, is applied)
- Levene test: test for homogeneity of variances (required to decide which subsequent statistical test, e.g. *t*-test, Welch-Test, is applied)
- *t*-Test and paired *t*-test: test for differences in means; applied when there is no indication that the data are not normally distributed and the variances are assumed to be equal
- Welch-Test: test for differences in means from two populations; applied when there is evidence that the variances of the data-sets are unequal
- Kruskal-Wallis test: test for differences in multiple means (non-parametric test); applied when there is evidence that the variances of the data-sets are unequal and the data are not normally distributed.

For all statistical tests a level of significance of 0.05 is used.

The overall trueness of the investigations achieved is estimated by applying statistical tests to the relative deviation from the theoretical value of all samples analyzed (52 in total).

2.6. Nested variance component analysis

Critical factors for a reliable determination of the biomass content in heterogeneous wastes and RDF include sampling, sample preparation and the chemical analysis itself. All steps are associated with errors and contribute to the variation observed for the final results. The total variance of replicate samples can be used to estimate the overall quality of the whole analysis (including sample conditioning). However, to find the cause for the scattered analyses data, the hierarchy of the variation's sources has to be investigated [36]. For this purpose analysis variances models with nested structure can be used as they allow the relative importance of the different sources of variation to be determined [37].

The variance component analysis (VCA) assumes that the variance of the results reflects the sum of the variances of all influencing factors and allows the total variation measured to be attributed to the single processing steps. A nested VCA, based on Hartung (1991) [38] and Sokal & Rohlf (2012) [37] is deployed for evaluating the random variation added by the four defined layers of sample preparation steps and the analysis itself. To do so, replicate samples are produced after each preparation step (see Fig. 3) and mean values are calculated at each layer.

Input of the variance component analysis (VCA) are the results after applying the adapted Balance Method, namely the parameter "Biogenic mass fraction" $x_{B,aBM}$, for each measurement conducted (five calculated values per sample).

As outlined in Fig. 3 and Table 2, altogether five layers of sample preparation and analysis are defined, namely (1) "Mixing and splitting", (2) "Cutting mill (<1 mm) & splitting", (3) "Milling (<0.2 mm) & splitting", (4) "Subsampling for analysis", and (5) "Analysis (error)", with the second layer nested within the first, the third layer nested within the second etc. The number of groups per layer is determined by the number of replications produced by sample splitting after each preparation step. For example, Layer "Mixing and splitting" only contains two groups as the sample is split into two parts after being mixed, whereas Layer (2) "Cutting mill (<1 mm) & splitting" includes six subgroups (samples △A and △B of Layer (1) are each split into three parts: ◇A, ◇B, ◇C) – see Fig. 3; note that the divided samples of each layer are illustrated in different shapes.

The variance components per layer are calculated as summarized in Table 2. The variation caused by a layer (e.g. variance component of Layer (1) σ_1^2) is estimated by summarizing the squared deviation between replications (e.g. $\overline{x}_{n_i}$ group means of Layer (1) for △A and △B) and the group means of the layer (e.g. $\overline{x}$ the total mean for ⬡A) and multiplying it by the sample size (replications) of the underlying layers. The computed sum of squares (SS) is divided by the degrees of freedom (represented by the denominator in the MS-equations in Table 2) to obtain the mean sum of squares (MS) per layer. The added variance component among the groups of a layer is estimated by comparing the MS between the groups of the respective layer (see Table 2; e.g. MS_1 represents the mean sum of squares for groups of Layer (1), namely △A and △B in Fig. 3) with the MS between the groups of the subsequent layer (e.g. MS_2 as MS of groups of Layer (2), namely ◇A, ◇B, ◇C in Fig. 3).

Negative estimators for σ^2 can occur when the variation at one layer decreases more strongly than expected by the variation of the subjacent layer (e.g. $MS_2 > MS_1$). Here, negative estimates are considered to be zero. The variation of the last layer reflects the variation within the measurements. As this layer contains both, the variation caused by drawing the five test specimens from the analysis sample and the variation of the analysis itself, two different factors are distinguished (Layer (4) and Layer (5)). Systematic errors from CHNSO-analysis are ruled out as regular calibrations and daily offset corrections are carried out. Thus the analysis error σ_5^2 is derived from the given device specifications (error term ε of Layer (5)). Layer (4) then accounts for the variance caused by "Subsampling for analysis" (σ_4^2).

The sum of squares for each layer add up to the total sum of squares SS_{tot}, which would also be obtained if the sum of squares of the entire data set is calculated.

The results are presented as variance components (σ^2) and their relative importance (σ^2 rel.) expressed as proportions of the sum of variance components. Furthermore, the coefficient of variation (CV) is determined for each layer, relating the variance component to the mean of the respective data set.

In order to test for significant differences between samples after each preparation step, F-values (F_s) can be computed as given in Table 2. The MS of each layer is related to the MS immediately beneath it. It can be tested whether the variation among the samples at a layer is higher

Table 2
Calculation of variance components at five layers (after [37,38]).

Source of variation	Variance component	Mean sum of squares (MS)	Sum of squares (SS)	F_s
Layer (1) Mixing & splitting	$\sigma_1^2 = \frac{MS_1 - MS_2}{n_2 * n_3 * n_4 * n_5}$	$MS_1 = \frac{SS_1}{n_1 - 1}$	$SS_1 = \sum_i^{n_1} n_2 * n_3 * n_4 (\overline{x}_{n_i} - \overline{x})^2$	$\frac{MS_1}{MS_2}$
Layer (2) Cutting mill (<1 mm) & splitting	$\sigma_2^2 = \frac{MS_2 - MS_3}{n_3 * n_4 * n_5}$	$MS_2 = \frac{SS_2}{n_1 * (n_2 - 1)}$	$SS_2 = \sum_i^{n_1} \sum_j^{n_2} n_3 * n_4 (\overline{x}_{n_i n_j} - \overline{x}_{n_i})^2$	$\frac{MS_2}{MS_3}$
Layer (3) Milling (<0.2 mm) & splitting	$\sigma_3^2 = \frac{MS_3 - MS_4}{n_4 * n_5}$	$MS_3 = \frac{SS_3}{n_1 * n_2 * (n_3 - 1)}$	$SS_3 = \sum_i^{n_1} \sum_j^{n_2} \sum_k^{n_3} n_4 (\overline{x}_{n_i n_j n_k} - \overline{x}_{n_i n_j})^2$	$\frac{MS_3}{MS_4}$
Layer (4) Subsampling for analysis	$\sigma_4^2 = \frac{MS_4 - MS_5}{n_5}$	$MS_4 = \frac{SS_4}{n_1 * n_2 * n_3 * (n_4 - 1)}$	$SS_4 = \sum_i^{n_1} \sum_j^{n_2} \sum_k^{n_3} \sum_l^{n_4} (\overline{x}_{n_i n_j n_k n_l} - \overline{x}_{n_i n_j n_k})^2$	$\frac{MS_4}{MS_5}$
Layer (5) Analysis (error)	$\sigma_5^2 = MS_5$	$MS_5 = (\varepsilon * \overline{x})^2$		
Total	$\sigma_{tot}^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \sigma_4^2 + \sigma_5^2$	$MS_{tot} = \frac{SS_{tot}}{n_1 * n_2 * n_3 * n_4 * n_5 - 1}$	$SS_{tot} = \sum_i^{n_1} \sum_j^{n_2} \sum_k^{n_3} \sum_l^{n_4} (\overline{\chi} - \overline{\chi} n_i n_j n_k n_l)^2 = SS_1 + SS_2 + SS_3 + SS_4$	

$\overline{x}$ = total mean.
$\overline{x}_{n_i}$ = mean of *i*-th group at Layer (1).
$\overline{x}_{n_i n_j}$ = mean of *j*-th group at Layer (2) (within *i*-th group of Layer (1)).
$\overline{x}_{n_i n_j n_k}$ = mean of *k*-th group at Layer (3) (within *j*-th group of Layer (2) within *i*-th group of Layer (1)).
$\overline{x}_{n_i n_j n_k n_l}$ = *l*-th analysis result at Layer (4) (within *k*-th group of Layer (3) within *j*-th group of Layer (2) within *i*-th group of Layer (1)).
n_1, n_2, n_3, n_4, n_5 = number of replications at Layers (1), (2), (3), (4), and (5).
ε = error for analysis estimated based on CHNSO device specification (0.9%).

than that to be expected on the basis of the observed variation among the samples of the subjacent layer. If the tested MS of a layer is larger than it is expected to be by chance (the case if the F_s-value is below the defined level of significance of 0.05), one can conclude that the differences among samples at the respective layer are significant [37].

3. Results and discussion

3.1. Overall assessment of the trueness of the biogenic mass fraction

The biomass content (biogenic mass fraction) of the prepared RDF model mixtures is determined by deploying the adapted Balance Method based on elemental analysis. The theoretical (true) value $x_{B,Theory}$ is determined from the predefined composition of the mixtures (see Table 1 and Supplementary material Eq. A.3).

The calculated biogenic mass fractions $x_{B,aBM}$ of mixture I and mixture II based on results per sample are presented in Fig. 4. The calculated values appear to be in good agreement with the theoretical values. No indication of differences between deviations from the theoretical value of mixture I and of mixture II can be found and the assumption that the data of both mixtures are normally distributed cannot be rejected (on a confidence level of 95%). Thus, the data of both data sets are combined and fitted to a normal distribution function, as shown in Fig. 4 b). Based on the assumption of normally distributed data, there is a probability of 95% that the pooled data are within 4.5%rel from the theoretical value. Moreover, it can be concluded that the results are underestimated by trend (around 0.6%rel) as the mean deviation in Fig. 4 b) is slightly below zero.

3.2. Overall assessment of the variation (repeatability) of the biogenic mass fraction

The variation of the observations for the biogenic mass fraction $x_{B,aBM}$ and thus the reproducibility of the whole method (sample preparation, chemical analysis and calculations according to the aBM) is estimated by calculating the standard deviation over the sample means. The maximum standard deviation found for the data sets of mixture I and mixture II is 1.7%abs (1.6%abs for mixture I and 1.7%abs for mixture II). This means that the sample values are scattered below ±3.0%rel around their mean.

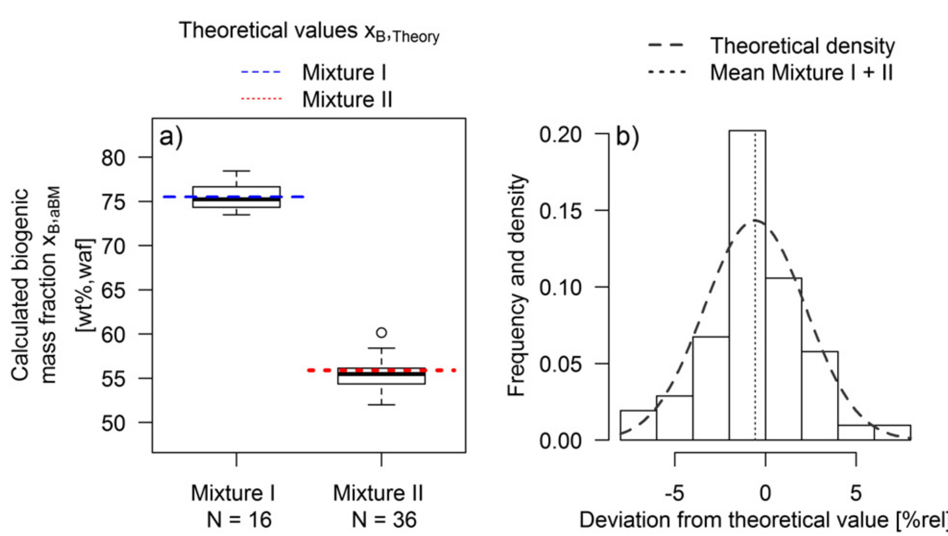

Fig. 4. a) Biogenic mass fraction $x_{B,aBM}$ of all samples (N…number of analysis samples) analyzed on a water-and-ash-free (waf) basis (for mixture I and mixture II) compared to the theoretical biogenic mass fraction $x_{B,Theory}$ of both mixtures; the outlier visible for mixture II may indicate improper homogenization but is not expected to cause an overestimation of the mean and is therefore retained; b) Relative frequency histogram and fitted normal density curve of the relative deviation from the theoretical value for results of mixture I and mixture II together.

3.3. Impact of different sample comminution on the trueness of the biogenic mass fraction

Table 3 summarizes the overall results for both RDF model mixtures. Besides the means and uncertainties of the biogenic mass fractions $x_{B,aBM}$ for each mixture, mean values (incl. standard deviation) for samples with a similar final conditioning step are also given. The calculated mean biogenic fraction on a water-and-ash-free basis (waf) for mixture I is 75.5 ± 1.6 wt% waf (with a theoretical value $x_{B,Theory}$ of 75.5 wt% waf) and for mixture II 55.4 ± 1.7 wt% waf (with a theoretical value $x_{B,Theory}$ of 55.9 wt% waf). Thus, a high accuracy of the mean (trueness) could be achieved. However small but significant differences between data sets can be observed when comparing results of samples finished with different mills (for both mixtures). This is not only the case for the aBM-output parameter "Biogenic mass fraction", but also for the aBM-input parameter TOC, TOH, and ash content (not presented here). The biogenic fraction for samples finally comminuted by a Cryomill solely appears underestimated by trend (−1.1 to −2.3%rel). Whereas, the samples treated with UCM show on average a 0.7 to 1.2%rel higher biomass content compared to the theoretical value. According to a *t*-test, only the deviations of Cryomill-finished samples are significantly different from zero (Table 3). It must be noted that the small sample size for the data sets of mixture I can easily influence the outcome of the significance test. However, the results clearly indicate that the sample preparation chosen may slightly change the sample composition (e.g. by thermal stress).

The mean deviation from the theoretical biogenic mass fraction (calculated as relative standard deviation) is lower for samples of mixture I (1.0–1.7%rel) compared to samples of mixture II (3.0–3.4%rel). This may partly be attributed to the lower biomass content of mixture II (absolute deviation is related to a lower mean), but also indicates that a higher complexity in terms of composition of the material mixture is more susceptible to changes in composition during sample preparation (mixture II contains a more heterogeneous material).

3.4. Variations in the biogenic mass fraction for different sample comminution

Significant differences in the variation of the results are observed when comparing samples of mixture I processed with different mills (Table 3). The standard deviation based on the mean values range from 0.7%abs (0.9%rel) for Cryomill-finished samples to 1.7%abs (2.2%rel) for UCM-finished samples. When mixture II is considered, the difference in standard deviation observed for samples with different final comminution is not significant, with 1.6%abs (2.8%rel) for samples with UCM + Cryomill conditioning and 1.4%abs (2.6%rel) for solely Cryomill-finished samples.

The diverse variances for samples with different final preparation steps are attributed to unequal grain size distributions within the analysis samples. When applying the UCM, cellulose fibers of paper and cardboard material in the mixtures are not completely destroyed and tend to agglomerate to particles larger than the desired 0.2 mm (visual observation and confirmed by sieve analysis conducted – see Supplementary material section E.). In contrast, the Cryomill crushes fibers to a large degree, but does not allow samples of defined particle size to be generated. Although the milling bin of the Cryomill is cooled with liquid nitrogen (−196 °C) to enhance crushing of elastic particles (rather than plating them), sieve analysis for samples milled via Cryomill show an accumulation of plastics in the larger grained fraction of the samples (see Supplementary material section E.; TOC and TOH increase with particle sizes and TOO decreases with particle size).

Comparing the results of the chemical analysis with the respective biomass content calculated via aBM demonstrates the distinct dependency of the biomass content on the elementary content of TOC, TOH and TOO (see Supplementary material: Fig. F.1 and F.2). Higher contents of organic carbon and organic hydrogen and lower contents of organic oxygen inevitably result in lower contents of biogenic matter and vice versa.

3.5. Assessing the impact of each preparation step on the variance of the biogenic mass fraction

In order to assess the impact of each preparation step on the variation observed for the final results, a variance component analysis (VCA) as a nested design is conducted based on equations in Table 2. Tables 4 and 5 present the results of the VCA for the parameter "Biogenic mass fraction" $x_{B,aBM}$ for mixture I and mixture II. Therein, variance components (σ^2), their relative importance (σ^2 rel.) as a percentage of total variation, the coefficient of variation (CV) as well as the results of the significance tests (*p*-values) are summarized.

Looking at the results for mixture I, the last milling step Layer (3) adds the most to the overall variance for UCM-samples as well as for

Table 3
Biogenic mass fractions determined by the adapted Balance Method $x_{B,aBM}$ compared to the theoretical biogenic mass fraction $x_{B,Theory}$ of both RDF model mixtures (given as mean value over results of the respective samples).

	Mixture I Paper:PE		Mixture II Paper:cardboard:PE:PET:PS	
	UCM-finished samples	Cryomill-finished samples	UCM + Cryomill-finished samples	Cryomill-finished samples
Theoretical biogenic mass fraction $x_{B,Theory}$ [wt% waf] ± SD	75.5 ± 0.3		55.9 ± 0.4	
Calculated biogenic mass fraction $x_{B,aBM}$ [wt% waf] (arithmetic mean ± SD)	75.5 ± 1.6		55.4 ± 1.7	
Calculated biogenic mass fraction $x_{B,aBM}$ [wt% waf] for samples with different finishing (arithmetic mean ± SD)	76.4 ± 1.7	74.7 ± 0.7	56.3 ± 1.6	54.6 ± 1.4
Result of 2-tailed *t*-test for differences in means / Levene test for differences in SD between samples with different finishing	*** / *		** / -	
Deviation of calculated value from theoretical value [%rel] $(x_{B,aBM} - x_{B,Theory})/x_{B,Theory}$ / results of 2-tailed *t*-test for differences from 0	+1.2% /	−1.1% / **	+0.7% / -	−2.3% / ***
Mean deviation of calculated value from theoretical value as RSD [%rel] = SD of $(x_{B,aBM,i} - x_{B,Theory})$	1.7%	1.0%	3.0%	3.4%
Number of samples	$N = 8$	$N = 8$	$N = 18$	$N = 18$

waf = water-and-ash-free.
$x_{B,aBM}$ = biogenic mass fraction on water-and-ash-free basis, determined by the adapted Balance Method (aBM).
$x_{B,aBM,i}$ = biogenic mass fraction on water-and-ash-free basis, determined for sample *i* by the aBM.
$x_{B,Theory}$ = biogenic mass fraction on water-and-ash-free basis, theoretical value based on the preset composition.
S D= standard deviation based on sample results.
RSD = relative standard deviation (SD related to the mean $x_{B,aBM}$).
N = number of samples (with 5 analyses for each sample).
Significance codes for t-test and Levene test -p > 0.1; 0.1 ≥ p > 0.05; * 0.05 ≥ p > 0.01; ** 0.01 ≥ p > 0.001; *** 0.001 ≥ p.

Cryomill-samples (relative variance components for Layer (3) 48.6% UCM-samples; 50.9% for Cryomill-samples). The p-values, with well below 0.05, indicate that there is a significant difference among the samples after the last milling and splitting step (confidence level of 95%).

The first mixing and milling steps Layer (1) and Layer (2) appear to not add significant variation to the final result (with p-values well above 0.05). The variance components, being zero (or negative) for these layers, could be caused by an insufficient number of replicates, leading to strong effects on the subsequent layers which might overlie the variance of Layer (1) and Layer (2).

The variance component of Layer (4) of the Cryomill-samples suggests that the results after the subsampling step do not differ significantly from each other (p-value > 0.05) and the added variance from this layer is significantly lower for Cryomill-samples (0.12) than for UCM-samples (4.03). It is expected that these findings result from better fiber destruction by the Cryomill, which facilitates representative subsampling for final analysis. Finally, Layer (5), which represents the analysis itself, shows a distinctly higher relative importance for the Cryomill-samples compared to UCM-samples (38.5% and 5.4%, respectively). However, the absolute variance component is more or less equal (0.45 and 0.47, respectively).

The visually observed phenomenon of fiber agglomerations after UCM-milling is assumed to add heterogeneity to the analysis samples, which is reflected in the results of the VCA. Table 4 shows that the overall variance is higher for UCM-samples (3.9%) compared to Cryomill-samples (1.4%). This is consistent with the findings in previous sections where the variance of the sample means is compared (see Section 3.4 and Table 3).

The results of the VCA for the conditioning and analysis of the five-component mixture II are summarized in Table 5. In comparison to the results for mixture I, the results are more complex and hence more difficult to interpret. The overall variance, expressed as a coefficient of variation (CV), is slightly higher for Cryomill-samples (3.1%) compared to samples prepared with UCM + Cryomill (2.9%). Comparing the variance of the single layers for the UCM + Cryomill-samples, there is a strong indication for an added variance component for each preparation step (p-values < 0.05). This means that in general all preparation steps cause "significant" changes in the sample composition with regard to the biomass content. Unexpectedly, a dominant influence of the first mixing and splitting step for UCM + Cryomill-samples (a relative importance of Layer (1) of 63.5%) is observed. This high variation caused by Layer (1) suggests that the mixing and first splitting (done at 4 mm grain size) did not lead to two equally divided parts. This could be caused by insufficient homogenization before the splitting or demixing effects due to insufficient particle size reduction. However, this finding is not confirmed by the results of the Cryomill-samples, where the first layer only adds a low variance component (with 6.6% related to the overall variation). In general, for the Cryomill-samples the first two preparation steps (Layer (1) and Layer (2)) did seemingly not lead to significant differences in sample results (p-values > 0.05).

Nevertheless, the initial mixing and splitting may represent a sensitive step for sample preparation, especially when more complex mixtures are concerned, but no distinct conclusions can be drawn as only two replications have been done at this layer.

For both mixtures a significant share of the overall variation originates from Layer (4), which represents the subsampling step where small specimens are drawn from the analysis sample to be fed into the elemental analyzer. The significantly lower absolute magnitude of the variance component of Layer (4) for UCM + Cryomill-samples (0.28) compared to Cryomill-samples (1.61) indicates that more homogenous samples are produced when both mills are applied. The lower variance component for UCM + Cryomill-samples is also evident when the respective variance components of Layer (3) are compared (0.13 for UCM + Cryomill-samples and 0.96 for Cryomill-samples). Thus, the application of both mills leads to a small variation of replicate measurements. It is assumed that the different grinding mechanisms of both mills destroy cellulose fibers (mainly by the Cryomill) as well as plastic particles (mainly by the UCM) to a large extent.

Comparing the variance components σ^2 of Cryomill-samples of mixture I to Cryomill-samples of mixture II (thus only comparing results for the two mixtures generated via the same sample preparation), it is apparent that the added variation from milling and especially from subsampling is higher for mixture II, which contains a higher fraction of fossil materials. This indicates once more that a proper destruction of plastic particles is crucial, in particular if they represent a high share in the mixture. Moreover, this outcome demonstrates that for mixtures that are more complex, subsampling for elemental analysis requires high experimental control and a sufficient number of replications is indispensable. A proper homogenization of the sample before analysis and a suitable method of drawing representative specimens from the analysis sample are essential. Both are obviously linked to the grain size and grain size distribution of the analysis sample.

Overall, the coefficients of variation (CV) of both mixtures are below 3% for all layers, which is regarded as a promising result and shows the general suitability of the sample preparation method applied in conjunction with the aBM.

Table 4
Results of the nested variance component analysis for the biogenic mass fraction $x_{B,aBM}$ of RDF model mixture I (obtained by the aBM).

	Source of variation (Layer)	Mixture I Paper: PE (79.4 wt%: 20.6 wt%, wf)									
		Parameter: Biogenic mass fraction $x_{B,aBM}$									
		UCM-finished samples					Cryomill-finished samples				
		σ^2	σ^2 rel. [%]	CV [%]	F_s	p-Value	σ^2	σ^2 rel. [%]	CV [%]	F_s	p-Value
				$n = 40$					$n = 40$		
(1)	Mixing & splitting	0[a]	0.0%	0.0%	0.02	0.896	0[a]	0.0%	0.0%	0.15	0.736
(2)	Cutting mill (<1 mm) & splitting	0[a]	0.0%	0.0%	0.90	0.475	0[a]	0.0%	0.0%	0.75	0.530
(3)	Milling (<0.2 mm) & splitting	4.26	48.6%	2.7%	5.74	0.001	0.60	50.9%	1.0%	6.17	0.001
(4)	Subsampling for analysis	4.03	46.0%	2.6%	9.57	0.000	0.12	10.6%	0.5%	1.27	0.233
(5)	Analysis (error) ε	0.47	5.4%	0.9%			0.45	38.5%	0.9%		
	Total	8.76	100.0%	3.9%			1.17	100.0%	1.4%		

σ^2 = variance component.
σ^2 rel. = relative variance component (related to the overall variance).
CV = coefficient of variation (related to the mean).
n = number of analyses (16 samples with 5 analyses each).
ε = error for analysis derived from device specification of CHNSO-analyzer (0.9%).
wf = water-free.
[a] Negative estimates for variance components are assumed to be zero.

Table 5
Results of the nested variance component analysis for the biogenic mass fraction $x_{B,aBM}$ of RDF model mixture II (obtained by the aBM).

	Source of variation (Layer)	Mixture II Paper: cardboard: PE: PET: PS (26.4 wt%: 34.3 wt%: 18.8 wt%: 10.3 wt%: 10.2 wt%, wf) Parameter: biogenic mass fraction $x_{B,aBM}$									
		UCM + Cryomill-finished samples					Cryomill-finished samples				
		σ^2	σ^2 rel. [%]	CV [%] $n = 90$	F_s	p-Value	σ^2	σ^2 rel. [%]	CV [%] $n = 90$	F_s	p-Value
(1)	Mixing & splitting	1.79	63.5%	2.3%	13.30	0.022	0.20	6.6%	0.8%	2.24	0.209
(2)	Cutting mill (<1 mm) & splitting	0.36	12.6%	1.0%	5.44	0.010	0.05	1.6%	0.4%	1.11	0.397
(3)	Milling (<0.2 mm) & splitting	0.13	4.7%	0.6%	2.22	0.019	0.96	31.2%	1.7%	3.57	0.000
(4)	Subsampling for analysis	0.28	9.8%	0.9%	2.05	0.001	1.61	52.2%	2.2%	7.2	0.000
(5)	Analysis (error) ε	0.26	9.3%	0.9%			0.26	8.4%	0.9%		
	Total	2.82	100.0%	2.9%			3.08	100.0%	3.1%		

σ^2 = variance component.
σ^2 rel = relative variance component (related to the overall variation).
CV = coefficient of variation (related to the mean).
n = number of analyses (36 samples with 5 analyses each).
ε = error for analysis derived from device specification of CHNSO-analyzer (0.9%).
wf = water-free.

3.6. Comparison of the aBM results to findings in other studies

Previous studies conducted by Fellner et al. (2011) [18] and Schnöller et al. (2014) [19] applying the aBM on 2-component mixtures revealed deviations from the theoretical value of <1%abs and 5%rel respectively. Thus, the found accuracy of the mean of the present study (4.5%rel deviation at a probability of 95%) is in a similar range of previous results and is competitive to results reported for standardized methods. For example, Ariyaratne et al. (2014), who analyzed the biomass content of predefined material mixtures (wood, paper, plastics) using the selective dissolution and the radiocarbon method (both methods described in EN 15440:2011), noted significantly higher deviations from the theoretical value (up to 7 and 16%, respectively) [39].

With respect to the repeatability, the obtained results indicate slightly lower variations (± 3%rel) compared to values in the literature (< ± 5%rel [18] and 4–5%rel [19]). In Schnöller et al. (2014), however, smaller test specimens were used (20 mg instead of 40 mg) and oxygen measurements were not considered [19]. The higher standard deviation in results for smaller test specimens supports the finding that the subsampling and analysis practice impair the variation of the aBM results.

Reported relative standard deviations of the biomass content for (real) refuse-derived fuels characterized by the selective dissolution method vary by ± 1.2% [8], below ± 2.5% [40], or ± 6.7% [9]. For the radiocarbon method Larsen et al. (2013) note a relative uncertainty in the range of 7 to 10% at a confidence interval of 95% when flue gas samples from a stack of a waste incineration plant are analyzed [15]. The results presented herein for the aBM are therefore clearly compatible and within the range of standardized methods for determining the biomass content of wastes.

4. Conclusions

The investigations conducted on two refuse-derived fuel (RDF) model mixtures (2-component and 5-component mixtures with 75.5 and 55.9% biogenic content, respectively) demonstrate the feasibility of the adapted Balance Method (aBM) for determining the biogenic mass fraction in heterogeneous material mixtures. At a probability of 95%, the calculated values deviate <4.5%rel from the preset (theoretical) biogenic mass fraction of the model mixtures, thereby demonstrating the trueness of the results.

In addition, a high level of repeatability for the analysis (including the sample preparation) is also proven as the relative standard deviation for the biogenic mass fraction of all samples analyzed is below ± 3.0%.

A small but significant effect of the sample preparation method chosen on the trueness and on the variation of the final results is observed when comparing samples comminuted with different mills. The biogenic mass fraction tends to be underestimated when the Cryomill is applied (up to minus 2.3% rel). The significant difference in standard deviation when different mills are compared is explained by the higher heterogeneity of the UCM-finished samples, which may be attributed to the agglomeration of fibers to bigger particles than the desired grain size of 0.2 mm.

The nested variance component analysis (VCA), which was already applied in previous studies for heavy metal data in waste incineration residues [36] or for metal flows in a mechanical-biological treatment plant [41], proves to be an appropriate tool to account for the complexity of the experiment and extract relevant information from it. For instance, it is shown that for both model mixtures the last milling step and the step of drawing the test specimens for analysis ("Subsampling for analysis") strongly affect the total variation observed for the biogenic mass fraction. This finding indicates that these particular steps require the greatest experimental control. Both are obviously linked to the grain size and grain size distribution of the analysis sample.

The lowest added variation due to milling and subsequent sampling for analysis is observed when the final preparation consists of a milling step by means of an UCM followed by a grinding process via Cryomill. This confirms findings from Smidt et al. (2008), who concluded on an improvement of reproducibility of analysis results for municipal solid waste when two mills with different working principles are applied in association [27].

In general, the choice of appropriate conditioning steps for the adapted Balance Method, should be based on the expected qualitative composition of the waste or RDF to be analyzed (for example, a rough approximation of the share of plastics and paper by visual inspection) together with the desired precision of the final result. Material mixtures with a high fraction of paper or cardboard primarily call for an adequate destruction of cellulose fibers (which, for example, a Cryomill is capable of) to avoid particle agglomeration. A further milling step (utilizing, for example, an UCM) to ensure a certain grain size for plastics might be practical when a high precision (error < 3%rel) is desired and the effort demanded is justifiable. When RDF with a rather high content of plastics are to be characterized, the precision is expected to be mainly influenced by the proper and assured crushing of the plastic particles.

As the performance of the mills applied appears limited, a combination of both types of milling processes (high-speed rotor mill, mixer mill) is proposed in order to facilitate a sufficient grinding of plastics and cellulose fibers to a grain size below 0.2 mm.

Acknowledgements

The authors would like to acknowledge the funding of the present study, which was provided by the Federal Ministry for Transport, Innovation and Technology (bmvit) and the Austrian Science Fund (FWF): [TRP 285-N28]. In addition, we would like to thank our laboratory team, particularly Stefan Spacek, for their support and laboratory analyses as well as Inge Hengl for graphical support.

Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.fuproc.2016.07.001.

References

[1] BMLFUW, Deponieverordnung 2008 (Landfill Ordinance 2008): 39, Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über Deponien. StF: Bundesgesetzblatt Teil II Nr. 39/2008, Austrian Federal Ministry of Agriculture, Forestry, Environment and Water Management 2008, p. 35 (www.ris.bka.gv.at).
[2] VÖZ, Nachhaltigkeitsbericht 2014 der österreichischen Zementindustrie (in German: Sustainability Report of the Austrian Cement Industry), Verein der österreichischen Zementindustrie VÖZ (Association of Austrian cement industry), Vienna, Austria, 2015 19.
[3] European, Parliament, Directive 2009/29/EC on amending Directive 2003/87/EC so as to improve and extend the greenhouse gas emission allowance trading scheme of the community, Off. J. Eur. Union (2009) 63–87.
[4] European, Parliament, Directive 2009/28/EC on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC, Off. J. Eur. Union (2009) 16–62.
[5] EN 15359:2011 Solid recovered fuels - Specifications and classes, European Committee for Standardization, CEN/TC343, 2011 21.
[6] ERFO, Standardisation of SRF - Basic information for producers and users of SRF, public authorities and other stakeholders, European Recovered Fuel Organisation (ERFO), 2013 8.
[7] EN 15440:2011 Solid recovered fuels - Methods for the determination of biomass content, European Committee for Standardization, CEN/TC343, 2011 62.
[8] QUOVADIS, in: C. Giovanni (Ed.), Quality Management, Organisation, Validation of Standards, Developments and Inquiries for SRF, CESI RICERCA, Milano, Italy 2007, p. 134.
[9] E.A. van Dijk, J.J. Steketee, Feasibility study of three methods for determining the biomass fraction in secondary fuels, TAUW bv, Deventer, Netherlands, 2002 51.
[10] J.G. Cuperus, E.A. van Dijk, R.C. de Boer, Pre-normative research on SRF, TAUW bv, Deventer, Netherlands, 2005 128.
[11] P.J. Kneissl, Method for Determining the Relationship of Renewable to Non-Renewable Sources of Energy, European Patent Office, Austria, 2001, pp. 21.
[12] W. Staber, S. Flamme, J. Fellner, Methods for determining the biomass content of waste, Waste Manag. Res. 26 (2008) 78–87.
[13] J. Fellner, O. Cencic, H. Rechberger, A New Method to Determine the Ratio of Electricity Production from Fossil and Biogenic Sources in Waste-to-Energy Plants, Environ. Sci. Technol. 41 (2007) 2579–2586.
[14] M. Obermoser, J. Fellner, H. Rechberger, Determination of reliable CO_2 emission factors for waste-to-energy plants, Waste Manag. Res. 27 (2009) 907–913.
[15] A.W. Larsen, K. Fuglsang, N.H. Pedersen, J. Fellner, H. Rechberger, T. Astrup, Biogenic carbon in combustible waste: Waste composition, variability and measurement uncertainty, Waste Manag. Res. 31 (2013) 56–66.
[16] J. Mohn, S. Szidat, J. Fellner, H. Rechberger, R. Quartier, B. Buchmann, L. Emmenegger, Determination of biogenic and fossil CO_2 emitted by waste incineration based on (CO_2)-C-14 and mass balances, Bioresour. Technol. 99 (2008) 6471–6479.
[17] T. Schwarzböck, H. Rechberger, O. Cencic, J. Fellner, Determining national greenhouse gas emissions from waste-to-energy using the Balance Method, Waste Manag. 49 (2016) 263–271.
[18] J. Fellner, P. Aschenbrenner, O. Cencic, H. Rechberger, Determination of the biogenic and fossil organic matter content of refuse-derived fuels based on elementary analyses, Fuel 90 (2011) 3164–3171.
[19] J. Schnöller, P. Aschenbrenner, M. Hahn, J. Fellner, H. Rechberger, Sample preparation and biomass determination of SRF model mixture using cryogenic milling and the adapted balance method, Waste Manag. 34 (2014) 2171–2175.
[20] P. Aschenbrenner, J. Fellner, H. Rechberger, in: K.J. Thomé-Kozmiensky, M. Beckmann (Eds.), Bestimmung des biogenen Kohlenstoffgehaltes von Ersatzbrennstoffen mittels eines CHNSO-Elementaranalysators (in German: Determination of the biogenic carbon fraction in refuse derived fuels by means of CHNSO elemental analysis), Erneuerbare Energien, Vivis Verlag, Neuruppin, Germany 2009, pp. 3–14.
[21] P.M. Gy, Sampling of Heterogeneous and Dynamic Material Systems, Theories of Heterogeneity, Sampling and Homogenizing, Data Handling in Science and Technology, vol. 10, Elsevier, Amsterdam, 1992.
[22] M. Prochaska, G. Raber, K.E. Lorber, Herstellung von Ersatzbrennstoffen (in German: Production of refuse derived fuels), Project Report, Conducted by Chair of Waste Processing Technology and Waste Management (AVAW) of Montanuniversitaet Leoben, on Behalf of Federal Ministry of Agriculture, Forestry, Environment and Water Management and Saubermacher Dienstleistungs AG, Leoben, Austria 2005, p. 104.
[23] M. Denner, I. Kügler, Erarbeitung eines Beprobunskonzeptes für Ersatzbrennstoffe (in German: Development of a sampling concept for refuse derived fuels), Project Report of Project ERSA, Report Number REP-0059, Umweltbundesamt GmbH (Federal Environment Agency Austria), on Behalf of Federal Ministry of Agriculture, Forestry, Environment and Water Management, Vienna, Austria 2006, p. 250.
[24] T. Schwarzböck, E. Van Eygen, H. Rechberger, J. Fellner, Determining the amount of waste plastics in the feed of Austrian Waste to Energy facilities, Waste Manag. Res. (2016) (accepted for publication).
[25] EN 15413, Solid recovered fuels - Methods for the preparation of the test sample from the laboratory sample, DIN Deutsches Institut für Normung e. V., 2011 39.
[26] D. Montané, S. Abelló, X. Farriol, C. Berrueco, Volatilization characteristics of solid recovered fuels (SRFs), Fuel Process. Technol. 113 (2013) 90–96.
[27] E. Smidt, K. Meissl, J. Tintner, The influence of waste sample preparation on reproducibility of thermal data, Thermochim. Acta 468 (2008) 55–60.
[28] M. Wilczek, J. Bertling, D. Hintemann, Optimised technologies for cryogenic grinding, Int. J. Miner. Process. 74 (2004) S425–S434 (Supplement).
[29] V. Gente, F. La Marca, F. Lucci, P. Massacci, E. Pani, Cryo-comminution of plastic waste, Waste Manag. 24 (2004) 663–672.
[30] T. Stehrer, J. Heitz, J.D. Pedarnig, N. Huber, B. Aeschlimann, D. Gunther, H. Scherndl, T. Linsmeyer, H. Wolfmeir, E. Arenholz, LA-ICP-MS analysis of waste polymer materials, Anal. Bioanal. Chem. 398 (2010) 415–424.
[31] EN 15414–3 Solid recovered fuels - Determination of moisture content using the oven dry method - Part 3: Moisture in general analysis sample, European Commitee for Standardization, 2011 14.
[32] EN 15403 Solid recovered fuels - Determination of ash content, European Committee for Standardization, 2011 10.
[33] DIN 51732 Testing of solid mineral fuels - Determination of total carbon, hydrogen and nitrogen - Instrumental methods, Deutsches Institut für Normung e. V., Berlin, Germany, 2014 10.
[34] R, Core, Team, A Language and Environment for Statistical Computing, R Foundation for Statistical Computing, 2013 (http://www.R-project.org/(Feb 2, 2015), Vienna, Austria).
[35] DataLab, Statistics Package, Epina GmbH, 2013 (http://datalab.epina.at (Dec 18, 2015), Pressbaum, Austria).
[36] G. Bauer, E. Schachermayer, Statistical analysis of heavy metal data from municipal waste incineration residues, Environ. Sci. Pollut. Res. 3 (1996) 10–16.
[37] R.R. Sokal, F.J. Rohlf, Biometry: The Principles and Practice of Statistics in Biological Research, W.H. Freeman and Co., New York, United States, 2012.
[38] J. Hartung, B. Elpelt, K.-H. Klösener, Statistik: Lehr- und Handbuch der angewandten Statistik, Oldenbourg Verlag München Wien, München, 1991.
[39] W.K.H. Ariyaratne, M.C. Melaaen, L.A. Tokheim, Determination of biomass fraction for partly renewable solid fuels, Energy 70 (2014) 465–472.
[40] M. Severin, C.A. Velis, P.J. Longhurst, S.J.T. Pollard, The biogenic content of process streams from mechanical-biological treatment plants producing solid recovered fuel. Do the manual sorting and selective dissolution determination methods correlate? Waste Manag. 30 (2010) 1171–1182.
[41] S. Skutan, P.H. Brunner, Stoffbilanzen mechanisch-biologischer Anlagen zur Behandlung von Restmüll (SEMBA) (in German: Material balances of mechnical-biological treatment plants for Residual Waste), Federal Ministry of Agriculture, Forestry, Environment and Water Management; Federal Environment Agency, Austria, Vienna, Austria, 2006 362.